

MAC 9693  
PATENT

## REMARKS

### A. Amendment

Claims 1, 23 and 46 are amended to require an article thickness of between about 5  $\mu\text{m}$  and 1000  $\mu\text{m}$ . Support for the amendment is provided at paragraph 36 of the specification.

Claims 5, 15, 20, 21, 28, 38, 43, 44, 51, 61, 66 and 67 are amended to require electromagnetic energy activation. Support is provided at paragraph 52 of the specification.

Applicants acknowledge the withdrawal of Corrigan (WO 00/03930) in support of the rejections under 35 U.S.C. §102(a) and 35 U.S.C. §103(a).

### B. The Opperman et al. (ZA 9602517) Reference

Because the full text of Opperman was not available, the Office cited the Derwent and CALPLUS abstracts. Applicants obtained the full text of Opperman and have attached a copy hereto.

### C. The Present Invention

The present invention is directed to gas generating and releasing articles, including monolayer articles, comprising a single polymer and a sulfur dioxide gas releasing solid (paragraphs 17 and 18), the article having a thickness of between about 5  $\mu\text{m}$  and 1000  $\mu\text{m}$  (paragraph 36). The articles are of sufficient strength to allow the preparation of gas releasing liners, sheets, shrink wraps, and even bags for containing products (paragraph 24). The articles function in the absence of an acid, a polymer that degrades to produce an acid, a compound that generates an acid in response to humidity, a hygroscopic compound, and an oxidant. Although a plasticizer may optionally be included in the formulations for purposes of, for example, softening and pliability, a plasticizer is not required for the claimed articles. Elimination and/or reduction in added amounts of components other than a polymer and gas releasing solid enables the preparation of high strength monolayers having high gas releasing solid loading and enhanced gas release characteristics by virtue of the reduced monolayer thickness. Only the present applicants have demonstrated that gas generating and releasing articles, such as films, having a

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thickness between about 5  $\mu\text{m}$  and 1000  $\mu\text{m}$  can be prepared. For instance, gas releasing films having a thickness of from about 50  $\mu\text{m}$  to about 125  $\mu\text{m}$ , from about 50  $\mu\text{m}$  to about 90  $\mu\text{m}$ , and from about 150  $\mu\text{m}$  to about 180  $\mu\text{m}$  were prepared in Example 2, films having a thickness of from about 25  $\mu\text{m}$  to about 75  $\mu\text{m}$  were prepared in Examples 3 and 4, and a film having a thickness of from about 50  $\mu\text{m}$  to about 100  $\mu\text{m}$  was prepared in Example 4.

**D. Rejection Under 35 U.S.C. §102(a)**

Reconsideration is requested of the rejection of claims 14-22, 37-45 and 60-68 under 35 U.S.C. §102(a) as being anticipated by Sanderson (WO 03/018431).

Claims 14-22, 37-45 and 60-68 depend from and include the limitations of claims 1, 23 and 46, respectively, all of which now require a (monolayer) article thickness of between about 5  $\mu\text{m}$  and 1000  $\mu\text{m}$  (i.e., 0.005 mm to 1 mm).

Sanderson describes a highly plasticized matrix of insufficient strength to form a gas releasing article. Sanderson teaches that such articles would lack strength and mechanical integrity and therefore must be supported by a carrier sheet and a cover sheet (page 6, line 11 to page 7, line 7). Sanderson does not describe articles, much less monolayer articles, having a thickness of between about 5  $\mu\text{m}$  and 1000  $\mu\text{m}$  (i.e., 0.005 mm to 1 mm). Although the gas releasing polymeric articles of the present invention may be optionally combined with other films, substrates, fabrics and the like to produce multi-layer films with specific characteristics needed for a particular use, as embodied in claims 14-22, 37-45 and 60-68, the articles are fully functional as a single polymer (or single polymer family) gas releasing article having a thickness of between about 5  $\mu\text{m}$  and 1000  $\mu\text{m}$  as embodied in claims 1, 23 and 46.

The Office states that the Sanderson carrier and/or cover sheets meet the limitations of claims 15, 20, 21, 38, 43, 44, 61, 67 and 68 since they would be expected to release a gas (at least through decomposition) upon exposure to a sufficient amount of energy. Sanderson does not describe gas generation and release upon exposure to any form of energy such as electromagnetic energy, as is now claimed.

It is respectfully submitted, therefore, that claims 14-22, 37-45 and 60-68 are patentable under 35 U.S.C §102(a) over Sanderson.

**MAC 9693  
PATENT****E. Rejection Under 35 U.S.C. §103(a) over Opperman**

Reconsideration is requested of the rejection of claims 1, 2, 4, 6-9, 13, 23, 24, 26, 27, 29-32, 36, 46, 47, 49, 50, 52-55 and 59 under 35 U.S.C. §103(a) as obvious over Opperman et al (ZA 9602517 A).

Opperman describes a device comprising a "plastics material" and a gas generating particulate. In particular: "[T]he reactants for the mixture include a polymer and a plasticizer. The plasticizer concentration in the reactants is preferably in the range from 35% to 45% by mass" (page 5, paragraph 3). Each Example includes a polymer in combination with 38 wt% (Examples 3-5) to 41 wt% (Examples 1-2) of a plasticizer. Opperman teaches that self-supporting gas releasing sheets must have a thickness of at least 1 mm (i.e., 1000  $\mu\text{m}$ ) and describes preparation of self-supporting sheets having a thickness of 1 mm to 3 mm, which may be cut into discs and attached to a backing (page 4, paragraph 6). Thicknesses of 2 mm to 3 mm are preferred (page 8, paragraph 3). A sheet having a thickness of 1 mm was prepared in Example 1 from which 30 mm discs were cut and attached to a backing support.

Opperman does not teach or suggest gas generating and releasing articles and monolayer articles comprising a gas generating and gas releasing article comprising between 30.0% and 99.9% by weight of a first polymer and between 0.1% and 70.0% by weight of a gas generating solid dispersed in the polymer and having a thickness of between about 5  $\mu\text{m}$  and 1000  $\mu\text{m}$  as is claimed. In fact, Opperman's teaching that self-supporting gas releasing sheets must have a thickness of at least 1 mm (i.e., 1000  $\mu\text{m}$ ) leads away from the present invention.

It is respectfully submitted, therefore, that claims 1, 2, 4, 6-9, 13, 23, 24, 26, 27, 29-32, 36, 46, 47, 49, 50, 52-55 and 59 are patentable under 35 U.S.C. §103(a) over Opperman.

**E. Rejection Under 35 U.S.C. §103(a) over Opperman in view of Aamodt (US Patent No. 6,325,969)**

Reconsideration is requested of the rejection of claims 3, 5, 25, 28, 48 and 51 under 35 U.S.C. §103(a) as obvious over Opperman in view of Aamodt (US Patent No. 6,325,969). Aamodt is relied upon for teaching a chlorine dioxide-releasing composition. It is said that it would have been obvious to use a combination of gas generating solids in the device of

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Opperman.

Aamodt does not overcome the deficiencies of Opperman. Aamodt describes a first porous paper product impregnated with a first chemical and a second porous paper product impregnated with a second chemical. Upon contacting the first and second paper products, the first and second chemicals react to produce an antimicrobial or biocidal chemical agent such as chlorine dioxide. Aamodt does not describe or suggest polymeric articles and does not suggest any advantage to modifying the teaching of Opperman to arrive at the articles of claims 3, 5, 25, 28, 48 and 51, the articles having a thickness of between about 5  $\mu\text{m}$  and 1000  $\mu\text{m}$ .

It is respectfully submitted, therefore, that claims 3, 5, 25, 28, 48 and 51 are patentable under 35 U.S.C §103(a) over Opperman in view of Aamodt.

**F. Rejection Under 35 U.S.C. §103(a) over Opperman in view of Steele et al. (WO 94/10233)**

Reconsideration is requested of the rejection of claims 10-12, 33-35 and 56-58 under 35 U.S.C. §103(a) as obvious over Opperman in view of Steele et al. (WO 94/10233). Steele is relied upon for sulfur dioxide producing polymeric films comprising polyvinyl chloride and low density polyethylene. It is said that it would have been obvious to substitute low density polyethylene for polyvinyl chloride in the Opperman device.

Steele does not overcome the deficiencies of Opperman. Steele describes single layer or multi-layer sulfur dioxide releasing films comprising a solid sulfur dioxide gas releasing compound, a polymer and at least one compound selected from a hygroscopic compound, an acid, a polymer that degrades to produce an acid or a compound that generates an acid in response to humidity. As the Office stated, Steele at page 4, lines 24-34 describes various polymers suitable for the preparation of gas generating and releasing polymer films. However, Steele does not suggest that that substitution of the PVC polymer of Opperman with, for example, low density polyethylene would result in gas generating and releasing films having a thickness of between about 5  $\mu\text{m}$  and 1000  $\mu\text{m}$ , nor would one skilled in the art have had any expectation that such a substitution would successfully result in reduced thickness.

It is respectfully submitted, therefore, that claims 10-12, 33-35 and 56-58 are patentable under 35 U.S.C §103(a) over Opperman in view of Steele.

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PATENT**CONCLUSION**

In view of the above, the invention defined in independent claims 1, 23 and 46 is respectfully submitted as patentable over the cited references. Claims 2-22, 24-45 and 47-68, which depend directly or indirectly from claims 1, 23 and 46, respectively, are likewise patentable over the cited art for the reasons stated with respect to claims 1, 23 and 46 and by reason of the additional requirements they introduce.

In light of the foregoing, applicants request entry of the amendments and withdrawal of the rejections under 35 U.S.C. §102(b) and 35 U.S.C. §103(a), and solicit allowance of the pending claims. The Examiner is invited to contact the undersigned attorney should any issues remain unresolved.

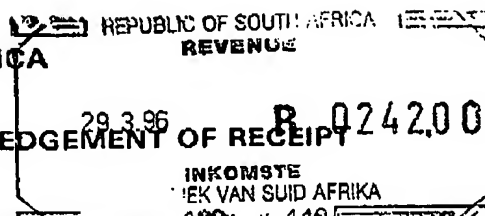
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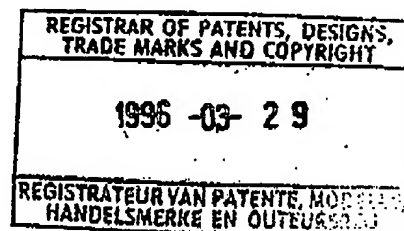
FORM P.1

**REPUBLIC OF SOUTH AFRICA**  
**PATENTS ACT 1978**

**APPLICATION FOR A PATENT AND ACKNOWLEDGEMENT OF RECEIPT**

(Section 30(1) - Regulation 22)

The granting of a patent is hereby requested by the undermentioned applicant on the basis of the present application filed in duplicate.

21 01 Official Application No.	96/2517	(i) Applicant's or agent's reference	U3-172
(ii) 71 Full name(s) of applicant(s)	RONALD DOUGLAS SANDERSON WILLEM JACOBUS OPPERMAN		
(iii) Address(es) of applicant(s)	Markotter Avenue 2, Stellenbosch Dagbreek Street 24, Stellenbosch		
(iv) 54 Title of invention	PRESERVATION DEVICE		
(v) The applicant claims priority as set out on the accompanying form P2. The earliest priority claimed is	ZA 94/7590 29 MARCH 1996		
(vi) 21 01 This application is for a patent of addition to Patent Application No:			
(vii) 21 01 This application is a fresh application in terms of section 37 and is based on Application No:			
(vii) This application is accompanied by:			
x	1.	Two copies of a complete specification of pages.	
x	2.	Drawings of sheets.	
x	3.	Publication particulars and abstract (Form P8 in duplicate).	
x	4.	A copy of Figure 4 of the drawings (if any) for the abstract.	
	5.	An assignment of the invention.	
	6.	Certified priority documents.	
	7.	Translation of the priority documents.	
	8.	An assignment of the priority rights.	
x	9.	A copy of Form P2 and the specification of SA Patent Appl. No.	
	10.	A declaration and power of attorney on Form P3	
	11.	Request for ante-dating on Form P4.	
	12.	Request for classification on Form P9.	
	13.		

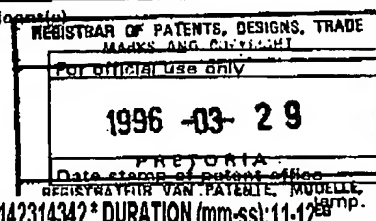


21	01	94/7590
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Dated this 29th March 1996

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FORM P:7

## REPUBLIC OF SOUTH AFRICA

PATENTS ACT, 1978

## COMPLETE SPECIFICATION

(Section 30(1) - Regulation 28)

OFFICIAL APPLICATION NO.		
21	01	96/2517

LODGING DATE	
22	1996 -03- 2 9

INTERNATIONAL CLASSIFICATION	
51	A23B 7/00

FULL NAME(S) OF APPLICANT(S)	
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FULL NAME(S) OF INVENTOR(S)	
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TITLE OF INVENTION	
54	PRESERVATION DEVICE

## BACKGROUND OF THE INVENTION

This invention relates to a method and means for preserving fresh produce.

The preservation of fresh produce from the time of packing until it reaches the point of sale has long been a problem in the fresh produce industry.

In the table grape industry, for example, sulphur dioxide (SO<sub>2</sub>) is the most common preservative used dating back to the late 1800's. During the early years of use, the packaged grapes were stocked in special rooms and gassed at intervals of a few days. This procedure had various negative effects on the quality of the grapes. This system was improved tremendously with the advent of in-package SO<sub>2</sub> generators, bringing the SO<sub>2</sub> into the closed grape box and closer to where it was needed, near the grapes. Much technical development has been done on the topic of in-package SO<sub>2</sub> production and many attempts have been made to try and find the best compromise between all the contributing factors.

Some previous work done in this field involved:



- The use of Poly(ethylene) bags to stabilise the emission of  $\text{SO}_2$  from metabisulphite solution.
- Poly(ethylene) coated Kraft paper containing sachets enclosing sodium bisulphite ( $\text{NaHSO}_3$ ) heat sealed together.
- Increasing the unit area of the  $\text{NaHSO}_3$  controlled-release device for better  $\text{SO}_2$  spread in the width and length of the grape pack.
- Emulsion of  $\text{NaHSO}_3$  with plastic polymers extruded as a thin layer on Kraft paper was effective as a first stage generator. Laminated emulsion casts releases  $\text{SO}_2$  only for short periods of time.
- Extrusion coated  $\text{NaHSO}_3$  polymer pastes using cellulose acetate films as moisture diffuser.
- Sachets with solid  $\text{NaHSO}_3$  gave efficient inhibition but no bleaching.
- Sachets with liquid potassium metabisulphite ( $\text{K}_2\text{S}_2\text{O}_5$ ) had less efficient inhibition but no bleaching occurred.
- Multipocket sachets overcoated with an emulsion coating of  $\text{NaHSO}_3$  for first stage generation.
- Multipocket system consisting of two sheets of grease proof paper glued together entrapping sodium metabisulphite ( $\text{Na}_2\text{S}_2\text{O}_5$ ).
- Poly(ethylene) sachets containing  $\text{Na}_2\text{S}_2\text{O}_5$  with silica with efficient inhibition but high bleaching injury high. It also produced irregular release rates.

According to Carlson (US Patent Number 3559562) the release rate of  $\text{SO}_2$  is proportional to its host particle size and recommended that a uniform release rate may be obtained from particles of a size distribution as follows: about 25 to 40 percent of the particles passing through a 100 mesh screen, but not through a 200 mesh screen; about 15 to 25 percent of the particles passing through a 200

mesh screen but not through a 325 mesh screen; and the remainder of the particles passing through a 325 mesh screen. This patent, from which SO<sub>2</sub> is liberated, involved the particulate compound being incorporated in a wax layer coated on a piece of paper.

The above reflects the vast amount of research that has been done on the topic of in-package SO<sub>2</sub> production to try and find the best compromise between all the contributing factors. Further developments are still being made.

#### SUMMARY OF INVENTION

According to a first aspect of the invention, a gas generating device for use in preserving fresh produce comprising a monolithic body having a first, matrix phase and a second, particulate phase uniformly dispersed within the first, the first phase being a plastics material and the second comprising a sulphur compound in particulate form and being capable of releasing a preservative gas when exposed to moisture.

The plastics material is preferably manufactured from reactants including a plasticiser and a polymer by means of a plastisol process. In such process, the plasticiser concentration in the reactants is in the range from 35% to 45% by mass and preferably is about 40% by mass.

In a preferred form of the invention, the polymer is polyvinyl chloride.

The concentration of the second, particulate phase in the body is generally in the range from 10% to 50% by mass, but is more preferably is in the range from 16% to 34% by mass.

The particulate, second phase compound is preferably a compound capable of releasing sulphur dioxide gas on exposure to moisture and is preferably a metabisulphite or bisulphite salt of an alkali metal. The salt should be non-toxic to humans.

In a further preferred embodiment, the reactants for the device further contain a stabiliser. When used, the stabiliser concentration in the reactants is in the range from 0.5% to 2% by mass.

The body, in a still further preferred form of the invention, includes means for promoting initial fast release of gas from it, followed by prolonged steadier release.

In a yet further preferred form of the invention, the promoting means comprises an humectant. Preferably the concentration of the humectant in the reactants is about 28% by mass.

The humectant is an hygroscopic polymer, which may be naturally occurring, such as starch, or synthetic, such as poly(vinyl)pyrrolidone.

In a still further preferred embodiment, the device has closed cells in a closed cell structure. At least some of the closed cells contain particles of the second phase material. The closed cells may result from including a blowing agent in the reactants. Where included, the concentration of blowing agent in the reactants is about 4% by mass.

In a further particularly preferred form of the invention, the body is a portion of a self supporting sheet. The thickness of the sheet is in the range from 1mm to 3mm. The sheet may be cut to form discs.

The device according to the invention may further including a backing and attachment means for attaching the backing to the body. The attachment means is preferably an adhesive and preferably the adhesive is a pressure sensitive acrylic adhesive.

The invention extends to a laminated structure comprising two or more of the monolithic bodies describes above, the bodies being connected by suitable joining means such as an adhesive or mechanical connecting means. Each of the bodies preferably has a different concentration of particulate second phase material in it.

According to a second aspect of the invention, a process for manufacturing a gas generating device for releasing a preservative gas for assisting in preserving fresh produce over an extended period when the device is exposed to moisture includes

the steps of providing reactants for making a plastics material, mixing the reactants together to form a homogeneous plastisol mixture, adding to the mixture a compound capable of releasing a preservative gas on being exposed to moisture, causing the compound to be dispersed generally uniformly throughout the mixture, forming into a sheet having sufficient thickness to be self-supporting when solidified and allowing it to solidify.

The process preferably includes the further step of dividing the solidified mixture into a plurality of monolithic bodies.

The reactants for the mixture include a polymer and a plasticiser. The plasticiser concentration in the reactants is preferably in the range from 35% to 45% by mass. More preferably the plasticiser concentration is about 40% by mass.

In a preferred form of the inventive process, the polymer is polyvinyl chloride.

In a still further preferred form of the invention, the concentration of the second, particulate phase in the device is in the range from 10% to 60% by mass and more preferably in the range from 16% to 50% by mass. The particulate compound is preferably capable of releasing sulphur dioxide on exposure to moisture and is preferably a metabisulphite or bisulphite salt of an alkali metal. Preferably the metal is sodium or potassium.

In an alternative preferred form of the invention, the process reactants further include a stabiliser. The stabiliser concentration in the reactants is preferably in the range from 0.5% to 2% by mass.

In a further preferred form of the invention, the reactants further include means for promoting initial fast release of gas from the device. Preferably the means comprises an humectant and the concentration of the humectant in the reactants is about 28% by mass. Preferably the humectant is an hygroscopic polymer, which may be selected from the group including starch and poly(vinyl)pyrrolidone.

In a yet further preferred form of the invention, the reactants include a blowing agent. The concentration of blowing agent in the reactants is about 4% by mass.

In the process, the mixing is preferably performed by means of a high speed stirrer operated at a stirrer speed in the range from 1000rpm to 2000rpm.

In a further preferred form of the invention, the mixture is cast into sheet form prior to being allowed to solidify.

In a still further preferred form of the process, the mixture is allowed to solidify by causing it to be baked. Preferably baking takes place at a temperature of less than 150 degrees Celsius. Still more preferably, baking takes place for a period of about five minutes.

The process may include the further step of forming the body into a disc. Furthermore, a backing means may be provided and attached to the body.

The invention extends to a method of preserving fresh produce comprising the steps of providing a device according to the description above, providing a container in which fresh produce is located, locating the device in the container, allowing moisture into the container and closing the container, so that on exposure of the device to moisture, it may cause a preservative gas to be released into the container. Preferably the gas is sulphur dioxide.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

FIGURE 1 illustrates schematically a cross-sectional view of a SO<sub>2</sub> generator manufactured according to the method described in example 1. (No additives)

FIGURE 2 illustrates schematically a cross-sectional view of a modified SO<sub>2</sub> generator manufactured according to the method described in example 3. (Blowing agent)

FIGURE 3 illustrates schematically a cross-sectional view of a modified SO<sub>2</sub> generator manufactured according to the method described in example 4. (Humectant and blowing agent)

FIGURE 4 is a schematic cross-sectional view across a vertical plane through a fresh grape container in which the generator of the invention is used.

FIGURE 5 is a graph showing the release rates of preservative gas released from devices according to the invention when PVP is included as an humectant.

FIGURE 6 is a graph showing the release rates of preservative gas released from devices according to the invention when starch is included as an humectant.

#### DETAILED DESCRIPTION OF THE EMBODIMENTS

The preservative gas generator shown in Figure 1 is generally designated 10 and comprises a body of monolithic plastics material providing a continuous, matrix phase 12 within which finely divided solute particles 14, which are generally uniformly dispersed, are contained, forming a second, discontinuous phase. Preferably the plastics material is polymeric, suitable examples being polyvinylchloride (PVC), polystyrene, polyethylene and the like. In a preferred form of the invention, PVC is used.

The monolithic device is prepared by incorporating the solute within powdered plastics resin material before plasticisation takes place. The process includes the steps of mixing together at high speed the reactants necessary to form a plastisol and adding thereto the solute particles and causing these to be dispersed therein, preferably by high speed mixing. Thereafter, the material may be cast into sheets and allowed to set, preferably by baking at a temperature below the thermal degradation temperature of the solute particles.

The body is preferably cut from a larger sheet of the plastics material and is monolithic in this sense. It may be an elongated strip or be any other suitable shape such as a disc, square, rectangle or triangle. In all these possible embodiments, the sheet material has sufficient inherent rigidity to be self-supporting in substantially a single plane and does not need a backing substrate.

The particulate compound 14 can be of any compound that releases the desired preservative gas upon contact with moisture, in particular, water vapour. Where the preservative gas is  $\text{SO}_2$ , the compound is preferably chosen from the group including sodium metabisulphite ( $\text{Na}_2\text{S}_2\text{O}_5$ ), sodium bisulphite ( $\text{NaHSO}_3$ ),

potassium metabisulphite ( $K_2S_2O_5$ ), although any other suitable alkali or alkaline earth metal salt may be used. On contact with water, there tends to be an initial rapid release of  $SO_2$  liberated from the compound, which, it is thought, is due to the absorption of water vapour in the atmosphere of the container and already in contact with the surfaces of the body. Thereafter follows a generally slower and steadier release over an extended period, which, depending on various factors to be discussed below, may last for an extended period - even up to 60 days.

The concentration of particulate compound 14 in the matrix phase 12 has an important effect on the release rate of the preservative from the device. Increasing the amount (concentration) of particles in the matrix phase 12 was found to increase the release rate since there is less polymer to inhibit the contact of the particles with water.

A further factor influencing the  $SO_2$  release rate and the release period is the thickness of the device. A thicker device will have the same release rate over the early stages of release, but over the latter stages it will be slower and more prolonged since the moisture takes a longer time to reach the particles as they are further removed from the exposed surface. For normal grape storage a suitable thickness has been found to be in the range of approximately 2 - 3 mm for release of  $SO_2$  for up to two months.

Referring to figure 2, where like numerals denote like components, another factor found to promote the rate of  $SO_2$  release is the presence of an humectant 16. Thus in a preferred embodiment there is included in the matrix a hygroscopic polymer as an humectant for attracting water, thus increasing the release rate. Suitable examples include starch and Poly(vinyl pyrrolidone) (PVP).

Referring to figure 3, the  $SO_2$  release rate and the release period may further be improved by the addition of a blowing agent (e.g. a chemical blowing agent) creating a structure of mostly closed cells 18 having an open porosity, thereby decreasing the density of the body. The blowing agent, in combination with the particulate compound 14 or with the blowing agent in combination with the particulate compound 14 and the humectant 16 increases the permeability of the matrix phase 12 to water vapour. The more permeable the material, the faster the  $SO_2$  release rate.

Referring to figure 4, the device 10 of the invention may be placed within the interior of a container 20 or package containing grapes, or any other fresh fruit, or the device may be attached to the rachis 22 of the grape bunch 24, by any suitable means. The bunch is enveloped in a gas tight wrapping 26, which is typically made of plastic sheet material e.g. poly(ethylene). The device may be coloured white or be pigmented and may be printed. Multilayered or laminated structures may be formed.

During storage, the grapes are placed in a cold storage room at low temperatures (approximately 0.5°C). As the relative humidity (RH) increases, the water reaches the particles on and near the surface of the matrix phase. A chemical reaction is thought to take place, releasing SO<sub>2</sub> into the container. The initial increase in SO<sub>2</sub> prevents the growth of molds e.g. *Botrytis cinerea*. The prolonged release of SO<sub>2</sub> over an extended period of time, such as over two months, is achieved as a result of the particles dispersed more deeply into the matrix phase 3 taking a longer time to be reached by moisture penetrating the matrix.

The release of solute gases from a granular matrix system is known to occur through connecting capillaries or pores. There is thus good reason to believe the mechanism of release is similar in a continuous matrix system of the present invention.

The monolithic sheets of the present invention may be structured to form multilayered monolithic devices for SO<sub>2</sub> release. Each layer may have a different solute particle concentration. The layers may be stacked to provide for a steady, controlled and predictable release of gas over a prolonged period, or for an initial high dose release followed by a slower sustained release. Mathematical expressions have been derived to describe the release of solutes from the matrix system. This system is expected to provide an easy-to-manufacture generator with a predictable release rate giving protection against fungi and molds for extended periods of time.

The following examples serve to describe several specific embodiments of the invention.



**Example 1**

A sulphur dioxide releasing device was manufactured according to the invention. A plastisol was prepared using the following formula:

PVC powder (K-value 80)	500g
Plasticiser (Dibutylphthalate) ("DBP")	350g
Stabiliser (Interstab <sup>™</sup> available from ACKROS Chemicals)	5g

The components were mixed together at high speed, approx 1000-2000 rpm., using a Heidolph overhead stirrer until a smooth homogeneous plastisol was obtained. To a 100 parts plastisol were added 50 parts sodium metabisulphite particles (CA grade) and mixed under high speed for 5 minutes to ensure a uniform distribution of the particles throughout the plastisol matrix. The plastisol mixture was cast into sheets approx. 1mm thick and baked in an oven at 145°C for 5 minutes.

The PVC sheets were removed from the oven and allowed to cool down before the discs, with an outside diameter of 30mm, were punched out. The discs are then used individually or may be attached, using an adhesive, such as pressure sensitive acrylic, to a plastic strip that allows it to be tied to the rachis (stem) of a bunch of grapes.

Eight of these discs containing 0.35g of sodium metabisulphite each, were then attached in this way to suitable bunches of grapes and covered in a plastic sheet envelope, in a standard corrugated carton box at ambient temperature. The boxes were then placed at approx. 1°C in a cold room for one month. Eight bunches are normally packed in such boxes.

To test for decay control efficacy, before the boxes were sealed, they were inoculated with (a) Dry *Botrytis cinerea* spores and (b) Berries with active growing *Botrytis cinerea*.

- (a) The spores were obtained from ten day old *Botrytis cinerea* cultures grown on Potato Dextrose Agar medium (PDA). A settling method was used in

order for natural infection and sporulation to take place under existing conditions. No water was used during this method.

- (b) Berries were inoculated by inflicting a small wound, approximately  $1\text{mm}^2$ , on the sterilised berry surface and inoculating it with spore suspension of approximately 50 000 spores per millilitre. Inoculated berries were placed in an incubator with an RH of approximately 95% and allowed to grow for one week prior to use. The seven day old berries were then placed amongst the other bunches of fruit (in the four corners) to obtain a spread to adjacent berries.

After the one month period the grapes were removed and kept at ambient temperature for four days prior to inspection.

The grapes were evaluated as follows:

- Total of mass of the grapes were determined.
- All the decayed berries, including the four used for inoculation, were removed and weighed and the percentage decay calculated.
- All the berries with  $\text{SO}_2$  damage calculated.

The quality of the grapes, used in the treatment, was compared to a control, where no  $\text{SO}_2$  was used. As a reference, standard dual  $\text{SO}_2$  sheets from Truroll/Grape Tech currently available to industry (quick release and 3g slow release sheets known as "std. + 3g sheets"), were used. the solute particles in these sheets are  $\text{NaHSO}_3$ .

The results obtained are shown in Tables 1 and 2 and indicate reduced decay in the grapes in respect of which the  $\text{SO}_2$  generator of the invention was used.

#### Example 2

The  $\text{SO}_2$  generator discs were manufactured in exactly the same way as in example 1 except that in this case two discs were attached to one another by

means of pressure sensitive acrylic adhesive. The two discs were identical except for the concentration of the particulate substance. One disc was manufactured using a plastisol mixture containing 20 parts  $\text{Na}_2\text{S}_2\text{O}_5$  to 100 parts plastisol by means, while in the second the ratio of  $\text{Na}_2\text{S}_2\text{O}_5$  to plastisol was 70:100. The discs were arranged in such a manner that the higher concentration had the largest exposed surface.

Eight of these discs containing approximately 0.58g of  $\text{Na}_2\text{S}_2\text{O}_5$  each were attached to bunches of grapes which were packed and tested according to the procedure in example 1.

The results obtained are also shown in Table 1 and 2.

### Example 3

Discs were manufactured in exactly the same manner as in example 1 except that in this case the plastisol formulation was altered to include a blowing agent to create a closed cell structure, but which provided it with an open porosity.

The formula used is as follows:

PVC (K-value 80)	56%
Plasticiser (DBP)	38%
Stabiliser	2%
Blowing agent (Genitron OB <sup>tm</sup> supplied by Schering Polymer Additives)	4%

To a hundred grams plastisol solution a hundred grams  $\text{NaS}_2\text{O}_5$  was added. Eight discs, each containing approximately 0.5g of  $\text{NaS}_2\text{O}_5$  were attached to grape bunches packaged in corrugated carton boxes and enveloped in a protective plastic sheet of poly(ethylene). The boxes of grapes were then stored at a temperature of approximately 0-2°C in a cold storage facility. The fruit were not inoculated with spores, unlike the case in example 1. This experiment was conducted only to determine the  $\text{SO}_2$  release rate of these devices. The gas concentration inside the package was monitored using a Picolog Datalogger system connected to a personal computer. Each of the detection cells was placed amongst the grapes in the centre region of a box. This system enabled the gas concentration inside the package to be determined without having any effect on the atmosphere inside the package.

**Example 4**

The discs were manufactured in exactly the same manner as in example 3 except that the plastisol formulation, used in example 3, was altered to include a humectant. The formulation used was as follows:

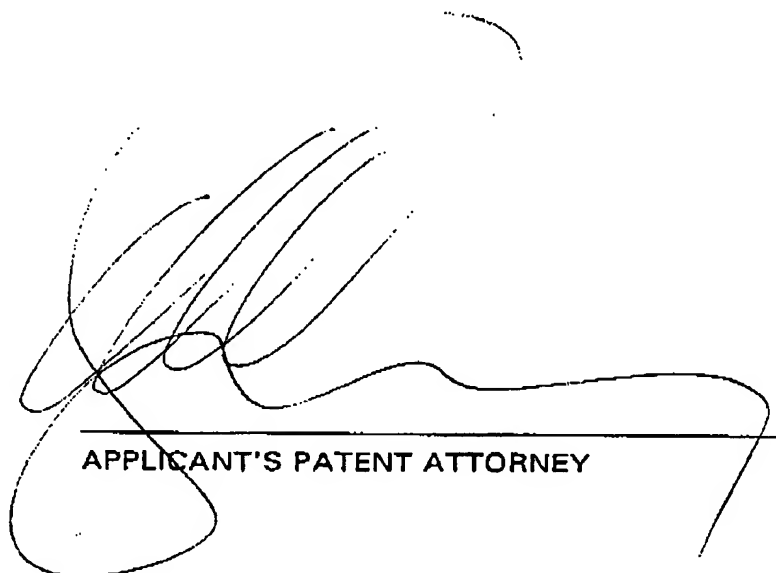
PVC (K-value 80)	28%
Plasticiser	38%
Humectant (PVP)	28%
Stabiliser (Interstab <sup>™</sup> )	2%
Blowing agent (Genitron OB <sup>™</sup> )	4%

The same evaluation procedure as was used in example 3 enabled the release rate depicted graphically in figure 5 to be determined. Compared with standard prior art S + 3g sheets, a steadier initial release rate is obtained.

**EXAMPLE 5**

Discs were manufactured according to the manner in example 4, except that starch was used as the humectant instead of PVP. The release rate of SO<sub>2</sub> observed is plotted in figure 6 and shows a longer sustained and steadier rate than the standard "S + 3g" sheets of the prior art.

SIGNED 29th March 1996



APPLICANT'S PATENT ATTORNEY

TABLE 1: Results obtained from dry spore inoculation.

TREATMENT	MASS (kg) INITIAL	DECAY MASS	% DECAY	AVG DECAY %	MASS SO <sub>2</sub> DAMAGED	% SO <sub>2</sub> DAMAGED	AVG % SO <sub>2</sub>
50 phr Example 1	5.225 5.205 5.310	0.180 0.135 0.395	3.445 2.594 7.439	4.492	0.135 0.095 0.095	2.584 1.825 1.789	2.066
20/70 phr Example 2	5.285 5.285 5.240	0.130 0.160 0.200	2.460 3.027 3.817	3.101	0.160 0.240 0.090	3.027 4.541 1.718	3.095
std + 3g Prior Art Standard	5.220 5.195 5.215	0.050 0.005 0.190	0.958 0.096 3.643	1.566	0.115 0.225 0.165	2.203 4.331 3.164	3.233
Control (No SO <sub>2</sub> )	5.320 5.305 5.220	2.065 2.595 1.935	38.816 48.916 37.069	41.600	0.000 0.000 0.000	0.000 0.000 0.000	0.000 0.000 0.000

phr : parts solute per hundred parts plastic resin

TABLE 2: Results obtained from berry inoculation.

TREATMENT	MASS (kg) GRAPES	DECAY MASS (kg)	% DECAY	AVG DECAY %	MASS SO <sub>2</sub> DAMAGED	% SO <sub>2</sub> DAMAGED	AVG % SO <sub>2</sub>
50 phr Example 1	5.345 5.020 5.220	0.395 0.180 0.295	7.390 3.586 5.651	5.542	0.220 0.145 0.085	4.116 2.888 1.628	2.878
20/70 phr Example 2	5.300 5.300 5.280	0.105 0.100 0.140	1.981 1.887 2.652	2.173	0.130 0.100 0.125	2.453 1.887 2.367	2.236
std + 3g Prior Art Standard	5.210 5.260 5.130	0.105 0.155 0.125	2.015 2.947 2.437	2.466	0.140 0.225 0.140	2.687 4.278 2.729	3.231
Control (No SO <sub>2</sub> )	5.310 5.340 5.350	0.870 0.925 0.800	16.384 17.322 14.953	16.220	0.000 0.000 0.000	0.000 0.000 0.000	0.000

phr : parts solute per hundred parts plastic resin

**CLAIMS**

- 1 A gas generating device for use in preserving fresh produce comprising a monolithic body having a first, matrix phase and a second, particulate phase uniformly dispersed within the first, the first phase being a plastics material and the second comprising a compound in particulate form and being capable of releasing a preservative gas when exposed to moisture.
- 2 A device according to claim 1 wherein the plastics material is manufactured from reactants including a plasticiser and a polymer by means of a plastisol process.
- 3 A device according to claim 2 wherein the plasticiser concentration in the reactants is in the range from 35% to 45% by mass.
- 4 A device according to claim 3 wherein the plasticiser concentration is about 40% by mass.
- 5 A device according to claim 4 wherein the polymer is polyvinyl chloride.
- 6 A device according to any one of the preceding claims wherein the concentration of the second, particulate phase in the body is in the range from 10% to 50% by mass.
- 7 A device according to claim 6 wherein the concentration of the particulate phase is in the range from 16% to 34% by mass.
- 8 A device according to any one of the preceding claims in which the compound is selected from the group including metabisulphite and bisulphite salts of alkali metals.
- 9 A device according to any one of the preceding claims wherein the reactants further contain a stabiliser.
- 10 A device according to claim 9 wherein the stabiliser concentration in the reactants is in the range from 0.5% to 2% by mass.

- 11 A device according to any one of the preceding claims wherein the body further includes means for promoting initial fast release of gas from it.
- 12 A device according to claim 11 wherein the means comprises an humectant.
- 13 A device according to claim 12 wherein the concentration of the humectant in the reactants is about 28% by mass.
- 14 A device according to claim 13 wherein the humectant is an hygroscopic polymer.
- 15 A device according to claim 14 wherein the hygroscopic polymer is a synthetic hygroscopic polymer.
- 16 A device according to claim 15 wherein the hygroscopic polymer is poly(vinyl)pyrrolidone.
- 17 A device according to claim 14 wherein the hygroscopic polymer is a naturally occurring hygroscopic polymer.
- 18 A device according to claim 17 wherein the hygroscopic polymer is starch.
- 19 A device according to any one of the preceding claims further having closed cells.
- 20 A device according to claim 19 wherein at least some of the closed cells contain particles of the second phase material.
- 21 A device according to claim 19 or claim 20 wherein the closed cells result from including a blowing agent in the reactants.
- 22 A device according to claim 21 wherein the concentration of blowing agent in the reactants is about 4% by mass.
- 23 A device according to any one of the preceding claims in which the body is a portion of a self supporting sheet.

- 24 A device according to claim 23 wherein the thickness of the sheet is in the range from 1mm to 3mm.
- 25 A device according to claim 23 or claim 24 wherein the body is in the form of a disc.
- 26 A device according to any one of the preceding claims further including a backing and attachment means for attaching the backing to the body.
- 27 A device according to claim 26 wherein the attachment means is an adhesive.
- 28 A device according to claim 27 wherein the adhesive is a pressure sensitive acrylic adhesive.
- 29 A process for manufacturing a gas generating device for releasing a preservative gas for preserving fresh produce over an extended period when the device is exposed to moisture includes the steps of providing reactants for making a plastics material, mixing the reactants together to form a homogeneous plastisol mixture, adding to the mixture a compound capable of releasing a preservative gas for preserving fresh produce on being exposed to moisture, causing the compound to be dispersed generally uniformly throughout the mixture, forming the mixture into a sheet having sufficient thickness to be self-supporting when solidified and allowing it to solidify.
- 30 A process as in claim 29 including the further step of dividing the solidified mixture into a plurality of monolithic bodies.
- 31 A process as in claim 29 or claim 30 in which the reactants include a polymer and a plasticiser.
- 32 A process as in claim 31 wherein the plasticiser concentration in the reactants is in the range from 35% to 45% by mass.



- 33 A process as in claim 32 wherein the plasticiser concentration is about 40% by mass.
- 34 A process as in any one of claims 29 to 33 wherein the polymer is polyvinyl chloride.
- 35 A process as in any one of claims 29 to 34 wherein the concentration of the second, particulate phase in the device is in the range from 16% to 50% by mass.
- 36 A process according to any one of claims 29 to 35 wherein the particulate phase comprises a bisulphite or metabisulphite salt of an alkali metal.
- 37 A process according to any one of claims 29 to 36 wherein the reactants further include a stabiliser.
- 38 A process according to claim 37 wherein the stabiliser concentration in the reactants is in the range from 0.5% to 2% by mass.
- 39 A process according to any one of claims 29 to 38 wherein the reactants further include means for promoting initial fast release of gas from the device.
- 40 A process according to claim 39 wherein the means comprises an humectant.
- 41 A process according to claim 40 wherein the concentration of the humectant in the reactants is about 28% by mass.
- 42 A process according to claim 41 wherein the humectant is an hygroscopic polymer.
- 43 A device according to claim 42 wherein the hygroscopic polymer is selected from the group including starch and poly(vinyl)pyrrolidone.

- 44 A process according to any one of claims 29 to 43 wherein the reactants include a blowing agent.
- 45 A process according to claim 44 wherein the concentration of blowing agent in the reactants is about 4% by mass.
- 46 A process according to any one of claims 29 to 45 wherein the mixing is performed by means of a high speed stirrer operated at a stirrer speed in the range from 1000rpm to 2000rpm.
- 47 A process according to any one of claims 29 to 46 wherein the mixture is cast into sheet form prior to being allowed to solidify.
- 48 A process as in claim 47 wherein the sheet has a thickness in the range from 1mm to 3mm.
- 49 A process according to any one of claims 29 to 48 wherein the mixture is allowed to solidify by causing it to be baked in an oven.
- 50 A process as in claim 49 wherein baking takes place at a temperature of less than 150 degrees Celsius.
- 51 A process as in claim 50 wherein baking takes place for a period of about five minutes.
- 52 A process according to any one of claims 29 to 51 including the further step of forming the body into a disc.
- 53 A process according to any one of claims 29 to 52 including the further step of providing a backing means and attaching the backing means to the body.
- 54 A gas generating device comprising two or more of the monolithic bodies according to any one of claims 1 to 28, joined together in a laminated structure.

- 55 A device according to claim 54 wherein the respective bodies contain different concentrations of particulate phase material.
- 56 A device according to claim 55 wherein the bodies are joined together with an adhesive.
- 57 A method of preserving fresh produce comprises the steps of providing a device according to any one of claims 1 to 28, providing a container in which fresh produce is located, locating the device in the container, allowing moisture into the container and closing the container, so that on exposure of the device to moisture, it may cause a preservative gas to be released into the container.
- 58 A device substantially as described herein with reference to any of the accompanying drawings.
- 59 A process substantially as described herein with reference to any of the accompanying drawings.
- 60 A method substantially as described herein with reference to any of the accompanying drawings.
- 61 A laminated device substantially as described herein.

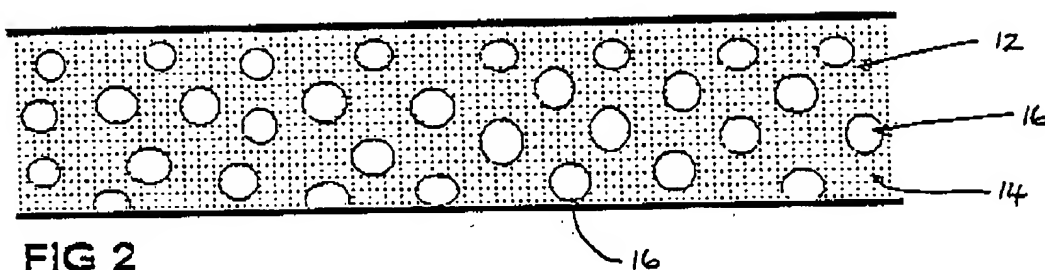
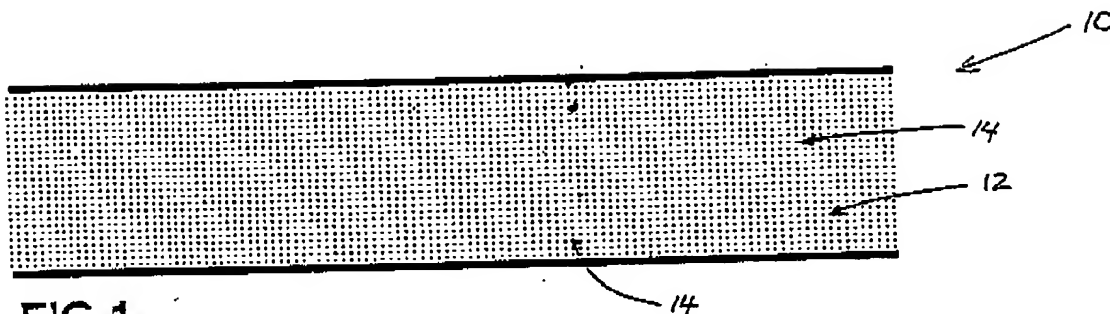
SIGNED 7th October 1996



APPLICANT'S PATENT ATTORNEY

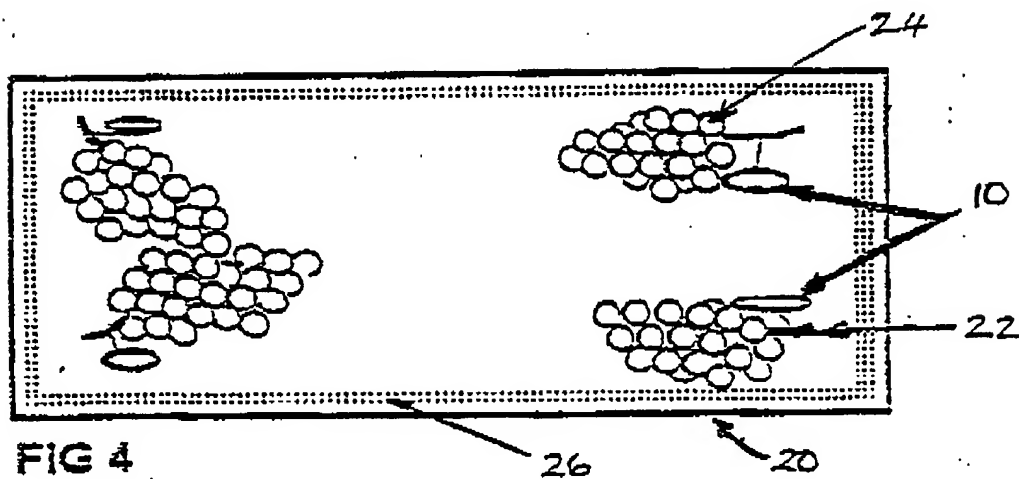
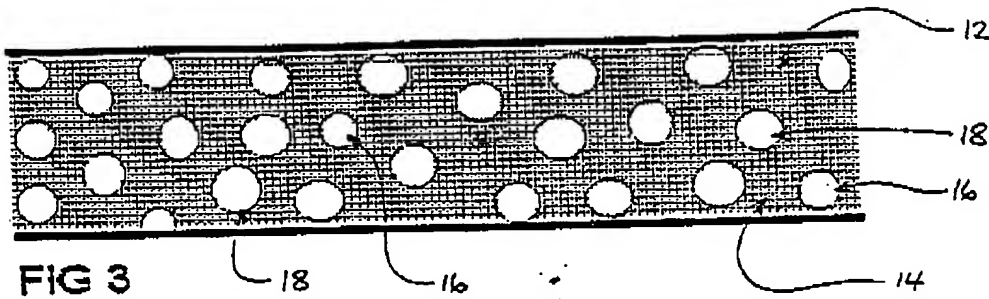
RONALD DOUGLAS SANDERSON  
WILLEM JACOBUS OPPERMAN

SHEET ONE  
THREE SHEETS



RONALD DOUGLAS SANDERSON  
WILLEM JACOBUS OPPERMAN

SHEET TWO  
THREE SHEETS



RONALD DOUGLAS SANDERSON  
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SHEET THREE  
THREE SHEETS

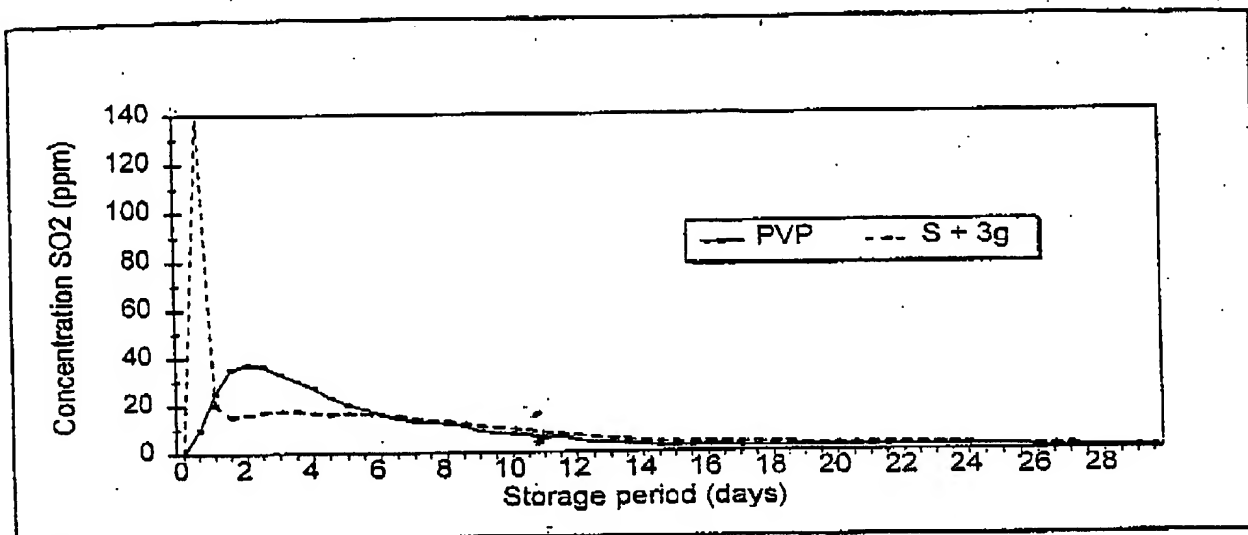


FIGURE 5

Release rate of SO<sub>2</sub> with PVP modified monolithic type device, compared to S + 3g sheets, over a storage period of one month.

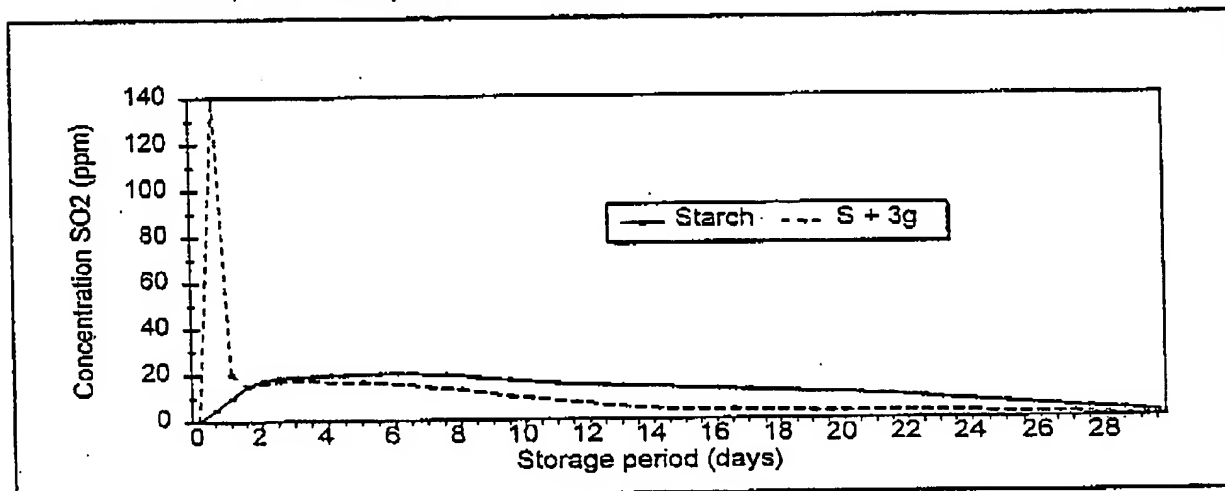


FIGURE 6

Release rate of SO<sub>2</sub> with soluble starch modified monolithic type device, compared to S + 3g sheets, over a storage period of one month.

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DECLARATION AND POWER OF ATTORNEY		INKOMSTE IEK VAN SUID AFRIKA	
(Section 30 - Regulations B, 22(i)(c) and 33)			

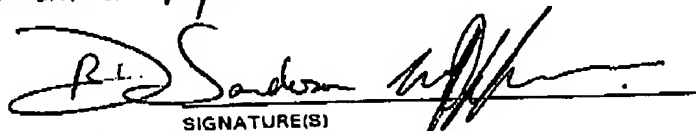
PATENT APPLICATION NO.		REF	LODGING DATE	
21	01	U3-172	22	
FULL NAME(S) OF APPLICANT(S)			REGISTRAR OF PATENTS, DESIGNS, TRADE MARKS AND COPYRIGHT	
71	RONALD DOUGLAS SANDERSON WILLEM JACOBUS OPPERMAN		10 APR 1996	
FULL NAME(S) OF INVENTOR(S)			REGISTRATEUR VAN PATENTE, MODELLE, HANDELSMERKE EN OUTEURSREG	
72	RONALD DOUGLAS SANDERSON WILLEM JACOBUS OPPERMAN			
EARLIEST PRIORITY CLAIMED		COUNTRY	NUMBER	DATE
		33 ZA	31 95/7590	32 29 MARCH 1995
TITLE OF INVENTION				
54	PRESERVATION DEVICE			

I/WE RONALD DOUGLAS SANDERSON and WILLEM JACOBUS OPPERMAN

hereby declare that:

1. I/We am/are the applicant(s) mentioned above;
2. I/We have been authorised by the applicant(s) to make this declaration and have knowledge of the facts herein stated in the capacity of the applicant(s);
3. the inventor(s) of the abovementioned invention is/are the person(s) named above and the applicant(s) has/have acquired the right to apply by virtue of an assignment from the inventor(s);
4. to the best of my/our knowledge and belief, if a patent is granted on the application, there will be no lawful ground for the revocation of the patent;
5. this is a convention application and the earliest application from which priority is claimed as set out above is the first application in a convention country in respect of the invention claimed in any of the claims; and
6. the directors and qualified staff of the firm of FAIRBRIDGE ARDERNE & LAWTON, attorneys at law, are authorised, jointly and severally, with powers of substitution and revocation, to represent the applicant(s) in this application and to be the address for service of the applicant(s) while the application is pending and after a patent has been granted on the application.

SIGNED AT Stellenbosch THIS 9 DAY OF April 19 96

  
SIGNATURE(S)